LUMINESCENCE SPECTRA OF ZINC OXIDE

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A study was made of the luminescence spectra of zinc oxide which first had been subjected to thermal processing at different temperatures. /224*

Introduction

On the basis of parallelism [1] in the change of the values of dark conductivity and the intensity of photoluminescence, established for zinc oxide, the conclusion was drawn that the same centers -- excess to the stoichiometric composition of zinc atoms -- are responsible for the luminescence and dark conductivity of ZnO. The hypothesis of the drift of electrons from the local levels of zinc atoms to the zone of conductivity, causing the temperature extinction of luminescence, led [2] to a dependence between the relative intensity I of luminescence and temperature T in the following form:

$$I = \frac{I_0}{1 + Ce^{-U/2kT}} \qquad (1)$$

where U is the distance from the levels of the zinc atoms to the zone of conductivity and C is a factor dependent on the excitation intensity.

It has been demonstrated [3] that the temperature extinction of luminescence of ZnO, subjected and not subjected to special thermal processing, is described by formula (1) and the distance from the zinc levels to the zone of conductivity, determined from the extinction curve, is in satisfactory agreement with the value of the activation energy determined from the temperature dependence of dark conductivity.

Using the first method, the following values were obtained for U: 0.36 EV for unheated ZnO, 0.47 EV for a sample heated to 500°C, and 0.5 EV for a sample heated to 600°C. The extinction of luminescence of samples heated to 630 and 730°C also was described by formula (1), but U changed in a jump from the values 0.36 EV at a low temperature to 0.6 EV at a high temperature for the first sample and from 0.8 to 0.6 EV for the second.

As an explanation of the latter result, it has been postulated that the luminescence spectra of ZnO samples first heated to 630 and 730°C consist of several bands whose extinction temperature is described by formula (1) with different values U and C. If the rate of extinction of different bands is not

*Numbers in the margin indicate pagination in the original foreign text.

identical, in the visual measurement of the temperature variation of luminescence we should obtain an extinction curve described by formula (1) with different values U at high and low temperatures. For the purpose of checking the correctness of the mentioned hypothesis, we studied the luminescence spectra of zinc oxide subjected to processing at different temperatures. The results are presented in this paper.

Experimental Results /225

The luminescence spectra corresponding to room temperature and at -180°C were photographed on panchromatic plates by a spectrograph with a glass optic. The 365 mμ mercury triplet was the exciting light. The phosphorus was cooled in a special Dewar vessel.

The spectral curves of luminescence at room temperature and the temperature of liquid air are shown in Figures 1 and 2. It can be seen that the spectral composition of luminescence of ZnO, unheated and heated to 500 and 600°, is the same; the spectrum contains only one band with a maximum at about 480 mμ. The heating of zinc oxide to 630°C causes the appearance of additional long-wave bands with maxima at about 525 and 560 mμ. Heating to 730°C enhances their brightness and causes the appearance of a fourth maximum at 670 mμ.

Figure 1. Spectral Curves of ZnO Luminescence at Room Temperature. Legend: 1 = Unheated ZnO; 2 = ZnO Heated to 630°C; 3 = ZnO Heated to 730°C.

Comparison of the curves in Figures 1 and 2 shows that with heating of ZnO samples from -180°C to room temperature the maxima of the spectral curves to all intents and purposes do not shift, but the long-wave bands at room temperature become exceedingly faint in comparison with the band at 480 mμ, that

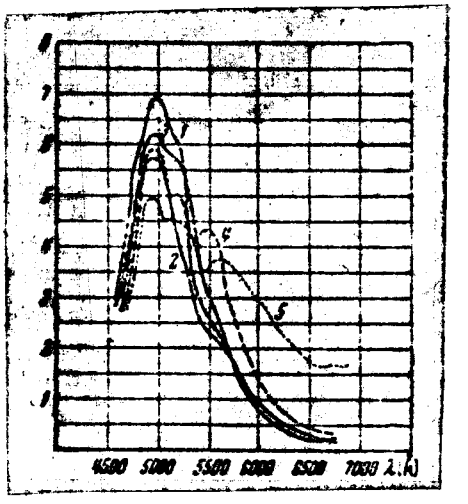

Figure 2. Spectral Curves of ZnO Luminescence at -180°C. Legend: 1 = Unheated ZnO; 2 = ZnO Heated to 500°C; 3 = ZnO Heated to 600°C; 4 = ZnO Heated to 630°C; 5 = ZnO Heated to 730°C.

is, the long-wave part of the spectrum is extinguished more rapidly during heating than the short-wave part. The latter circumstance explains the change of color of luminescence of the sample heated to 730° from golden-yellow at the temperature of liquid air to lettuce-green at room temperature. Conversion of the spectral distribution of luminescence of this sample, with the visibility curve (Figure 3) taken into account, shows that at a low temperature the 560 mμ-band is brightest, but at room temperature and above, the 525 mμ-band is brightest. Therefore, visual measurement of the extinction of this sample should give a dependence described by formula (1) with a value U characteristic for the 560 mμ-band at a low temperature and for the 525 mμ-band at room temperature and above.

It was mentioned above that for a sample heated to 730°C such a picture /226 in fact is observed.

Discussion of the Results

Four bands were discovered in the ZnO luminescence spectrum. If it is assumed that they are emitted as a result of transition of electrons from local levels of different depth into the main zone, the distance from these levels to the zone of conductivity can be computed by comparing the absorption and luminescence spectra. It follows from the measurements of the long-wave limit of the fundamental absorption band made by Gisolf [4] and ourselves [5] that the width of the ZnO forbidden band is 3.20 EV. By subtracting from this value the energy of the maximum of the luminescence bands, we find the distance from the local levels to the conductivity zone: 0.6, 0.8, 1.0 and 1.2 EV.

In the study of the dark conductivity of ZnO subjected to different

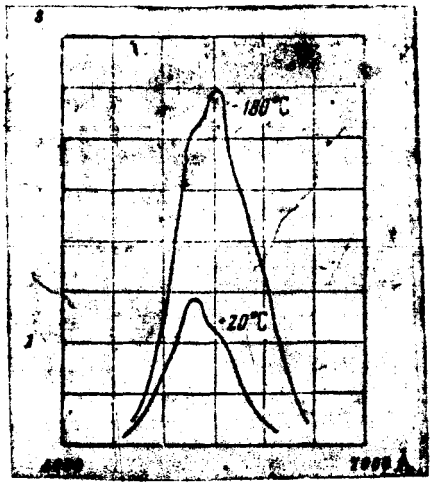

Figure 3. Luminescence Spectra of ZnO Heated to 730°C, with the Visibility Curve Taken into Account.

temperature processings [10] it also was possible to detect energy levels of excess atoms of zinc, situated at the depths: 0.4, 0.5, 0.6, 0.8, 1.0 and 1.4 EV.

Measurements of the temperature extinction of luminescence also are evidence of the presence of local levels of different depth in the forbidden zone.

Table 1 gives a comparison of the values U obtained from the temperature dependence of dark conductivity, from measurements of the extinction of luminescence and from the radiation and absorption spectra.

TABLE 1.

1 Значение U (eV), получ. из измерений:		
2 [illegible] проводимости	3 температурного гашения люминесценции	4 из спектров излучения и поглощения
0,4	0,36	0,6
0,5	0,5	
0,6	0,6	0,8
0,8	0,8	1,0
1,0	[illegible]	1,2

Legend: 1 = Value U (EV), Obtained from Measurements; 2 = Dark Conductivity; 3 = Temperature Extinction of Luminescence; 4 = from Radiation and Absorption Spectra.

The table shows that the values of the activation work U, determined for different samples from the temperature dependence of conductivity and luminescence, are less than the corresponding values obtained from a comparison of the radiation and absorption spectra.

If it is assumed that each local level detected during measurement of the dark conductivity should cause some luminescence band, it may be expected that there will be an infrared band with a maximum at about 770 mμ for ZnO. A search now is being made for this band.

Conclusion /227

A study of the luminescence spectra of zinc oxide subjected to different temperature processings revealed that in samples for which the extinction of luminescence is described for formula (1) with different values U at high and low temperatures the radiation spectrum contains several bands; it contains one band if the extinction curve corresponds to one value U at high and low temperatures.

It is shown that the luminescence spectra of zinc oxide can be changed by heating the ZnO at different temperatures. This fact confirms the communication by Kutselnigg [7], where he states that the color of luminescence of ZnO is dependent on the method for obtaining it and on prior thermal processing.

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